Influence of the platform in multicoordinate ligands for actinide partitioning

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Multicoordinate ligands based on the trityl, C-pivot, and CTV platforms and the ligating groups CMPO, DGA, PICO, and MPMA were synthesized and studied for their extraction properties. The extraction efficiencies of these multicoordinate ligands are largely influenced by the properties of the platform. The D_{Am} values follow the order CTV6 > trityl ≈ C-pivot > CTV3 > CTV0 with a maximum for CTV6CMPO of D_{Am} = 30 ($S_{Am/Eu}$ = 1.4, c_L = 10^{-4} M, 3 M HNO_3). There is a strong relationship between the D_{Am} values, increasing in the order of CTV0CMPO < CTV3CMPO < CTV6CMPO, and the 'mobility' of their CMPO groups. The $S_{Am/Eu}$ values are less influenced by the platform and range between 0.2 and 2.0, though they can reverse under the influence of the HNO_3 concentration (CTV6PICO $S_{Am/Eu}$ = 0.7 at 0.001 M HNO_3 to 1.2 at 0.01 M HNO_3) or by changing the platform (CTV(0, 3 or 6)MPMA from $S_{Am/Eu}$ = 0.4 to 1.6 for tritMPMA both at 0.001 M HNO_3). For the CMPO derivatives the $S_{Am/Eu}$ values are most consistent, ranging from 1.4 to 1.8.

Introduction

Minor actinides *i.e.* Np, Am, and Cm are responsible for the long-term radiotoxicity of HLLW (High Level Liquid Waste) nuclear waste. The radiotoxicity of these long-lived ($t_{1/2}$ = 10^2–10^6 years) nuclides can be reduced *via* transmutation into short-lived ($t_{1/2}$ = 10^1 years) nuclides or stable nuclides. Separation (partitioning–transmutation strategy (P & T))[1,2] of these actinides from the relatively harmless lanthanides is essential to success in the transmutation process.

In current industrial separation processes, trivalent Am and Cm will always be extracted together with lanthanides and this complicates the transmutation.[3] Improvement of the efficiency of the actinide (An(III))–lanthanide (Ln(III)) separation will therefore increase the feasibility of the currently impractical waste reprocessing.

A strategy to obtain Am^{3+} ligands having both high $S_{Am/Eu}$ (separation) and D_{Am} (distribution) ratios is by preorganizing existing 'hard oxygen donor' ligating groups onto a platform. The advantage of using such multicoordinate ligands containing hard donor atoms is that the increase in $S_{Am/Eu}$ value coincides with generally high D_{Am} values which are retained at higher acidities (3 M HNO_3). Very recently this strategy has been reviewed.[4]

Here the Am^{3+} and Eu^{3+} extraction properties of multicoordinate ligands based upon the trityl, cyclotriveratrylene (CTV), and C-pivot platforms (Chart 1) and four known Am^{3+} ligating groups *viz.* CMPO (diphenyl carbamoylmethyl)phosphine oxide),[5,6] PICO (picolinamide),[7] DGA (*N*,*N*′-dimethyl diglycoldiamide),[8] and MPMA (*N*-methyl-*N*-phenylmalonamide)[9] are described. Multicoordinate ligands based on these ligating groups and the calix[4, 6, and 8]arene and cavitand platforms are known.[4] In contrast to these platforms, the ones described here are functionalized with three ligating groups. This number matches the 1 : 3 metal : ligand stoichiometry that was found for CMPO groups that are not preorganized.[5]

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Results and discussion

Synthesis

Trityl based multicoordinate ligands. The trityl (triphenoxymethane) platform can be conformationally locked, such that the three hydroxyl groups point into the same direction, by substituting the *m*-position of the benzene ring with a (sterically) bulky group (Chart 1).[10] It has been shown that the trityl platform is able to tightly place ligating groups together to provide a good fit for the complexation of Eu^{3+}.[10] Due to the bulky *tert*-butyl groups the hydroxyl groups of **4** are sterically hindered and consequently are less reactive. By reaction of these phenol moieties with the reactive chloroacetonitrile and subsequent reduction with $LiAlH_4$ trityl **6** can be obtained in two steps in an overall yield of 68% as reported in the literature.[10] Optionally, trityl **5** was reduced to **6** using BH_3 in refluxing THF. Due to the $-(CH_2)_2-$ spacer the connecting points (amino moieties) are less sterically crowded, and in addition the reactivity is increased as compared to the original hydroxyl groups (Scheme 1).

Trityl **6** was functionalized with the CMPO, DGA, and PICO ligating groups by reaction with their *p*-nitrophenol activated esters (Scheme 2). The MPMA ligating group was connected to the trityl by using an activated amide coupling, since the syntheses of its *p*-nitrophenol activated ester was unsuccessful. In the ^1H NMR spectra the triplets of the two

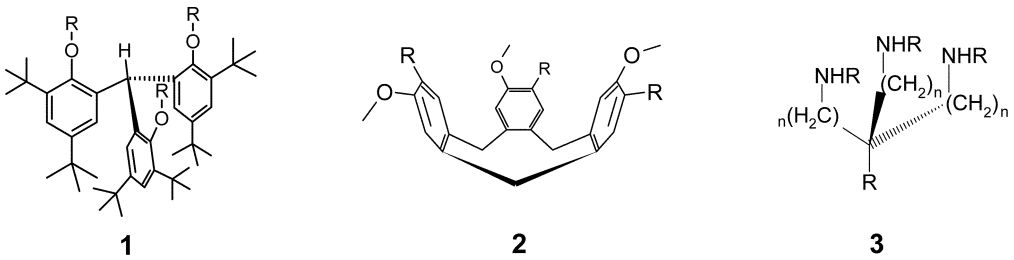
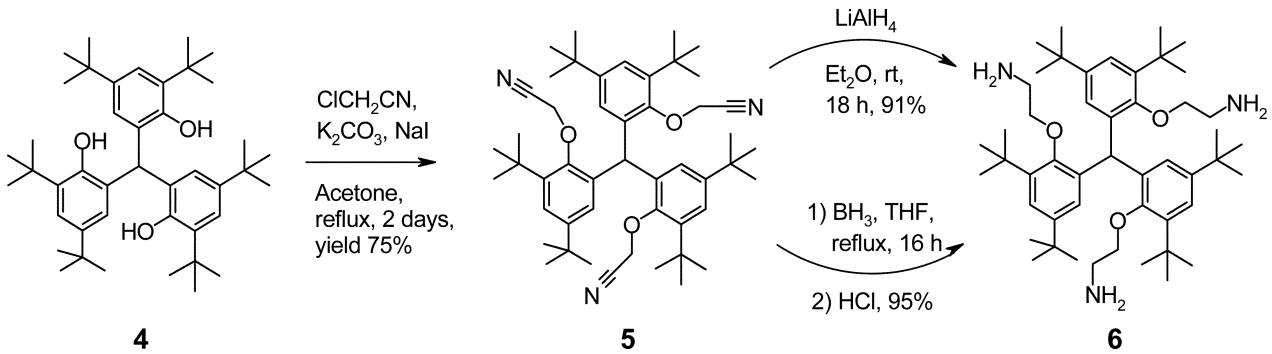


Chart 1 3D representations of the trityl, CTV, and C-pivot platforms.

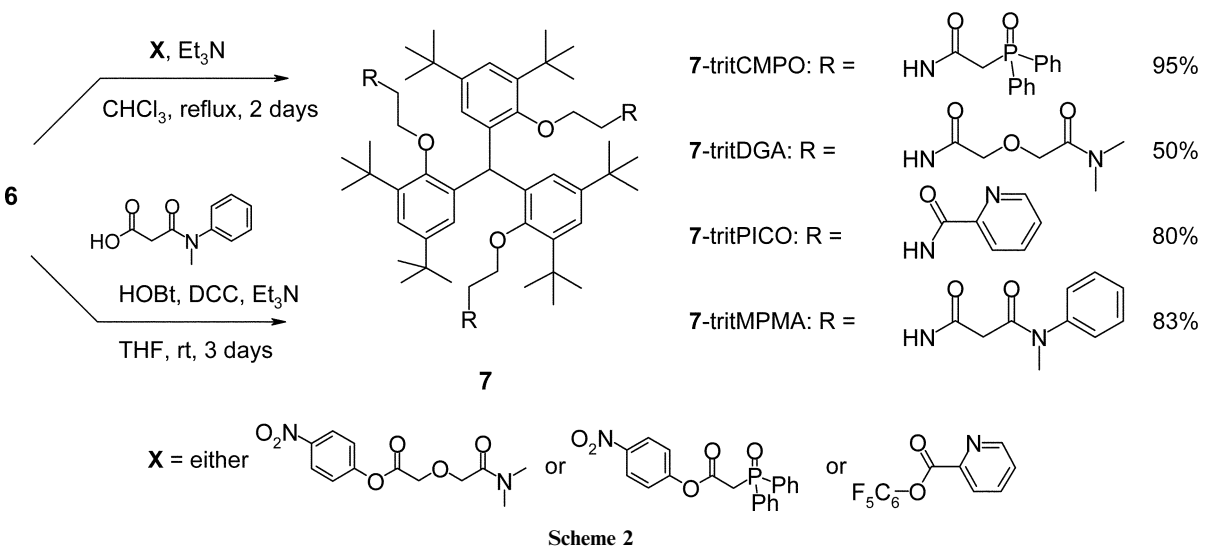


Scheme 1

–CH_2– groups of the spacer in the multicoordinate ligands **7**–CMPO, **7**–DGA, **7**–PICO, and **7**–MPMA are often broad and poorly resolved due to their close proximity and the sterically crowded environment.

CTV based multicoordinate ligands. The stable crown isomer of the CTV (cyclotriveratrylene, also called cycloveratril) macrocycle has its functional groups oriented towards one side of the molecule and can be functionalized with three ligating groups.[11,12] The length of the –$(CH_2)_n$– spacer between the ligating groups and the platform determines the mobility and consequently the degree of preorganization of the ligating groups. Three CTV platforms having different –$(CH_2)_n$– spacer lengths were synthesized. These include the **8**–CTV0 platform which induces a rather tight preorganization of its ligating groups, the **11**–CTV3 platform having –$(CH_2)_3$– spacers, and the **13**–CTV6 platform equipped with –$(CH_2)_6$– spacers which results in very mobile ligating groups (Chart 2).

The amine CTV **8**[13] (Chart 2) and the phenolic CTV **9**[14] were prepared *via* the well known perchloric acid catalyzed condensation of 3,4-disubstituted benzyl derivatives according to literature procedures.[15,16] For the latter condensation reaction the perchloric acid was diluted with MeOH. The phenolic CTV **9** was used as starting compound for the synthesis of CTVs **11** (Scheme 3) and **13** (Scheme 4). Reaction of **9** with *tert*-butyl-*N*-(3-bromopropyl)carbamate gave the BOC protected CTV **10** in 86% yield. The BOC groups were cleaved using TFA to give the TFA-salt **11a** upon precipitation from Et_2O. The salt was used in subsequent reactions since deprotonation of the salt using 1 M NaOH to its amine form **11** reduces the yield to 77%.



Scheme 2

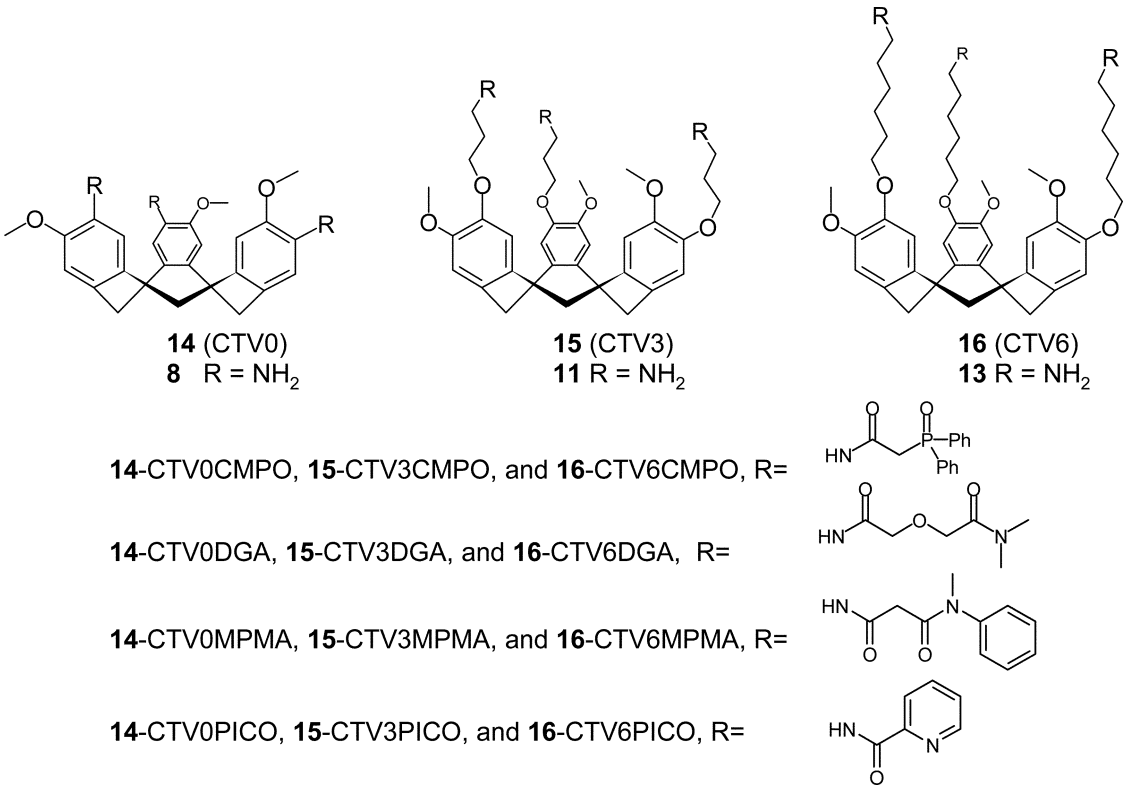


Chart 2 Synthesis of multicoordinate ligands based on the **8**–CTV0, **11**–CTV3, and **13**–CTV6 platforms.

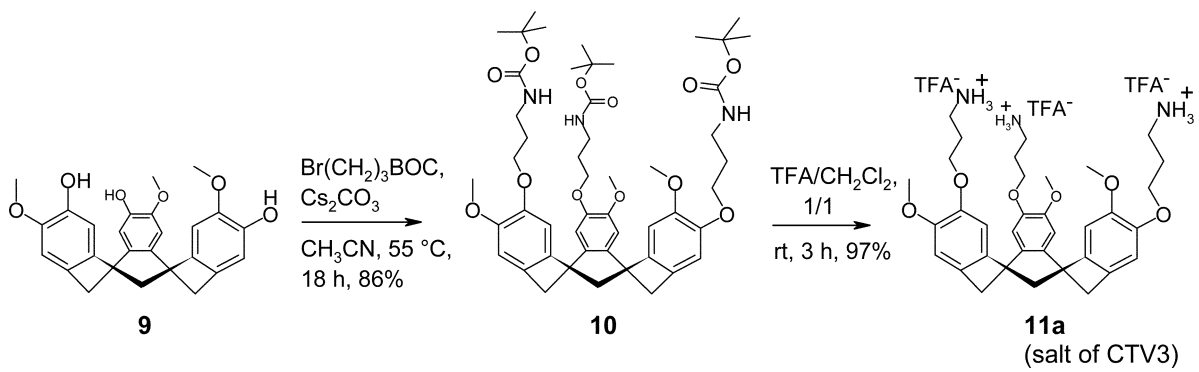
The synthesis of CTV **12** was performed by reaction of **9** with 6-bromohexanenitrile using caesium carbonate as a base to give CTV **12** in 91% yield. Firstly, the reduction of **12** to its amine CTV **13** was attempted using BH_3 in refluxing THF. However, the decomposition of the CTV **13**-BH_3 adduct was very difficult, resulting in low yields. Raney-cobalt in combination with 7 bar of H_2 at room temperature was successful and gave CTV **13** in 93% yield.

The CTV based multicoordinate ligands (Chart 2) were synthesized by reaction of the amino terminated CTVs with either the activated ester of the respective ligand (CMPO, DGA and PICO) or *via* an activated amide coupling (MPMA). The reaction of CTV0 with the activated ester of PICO yielded an insoluble product which could not be purified.

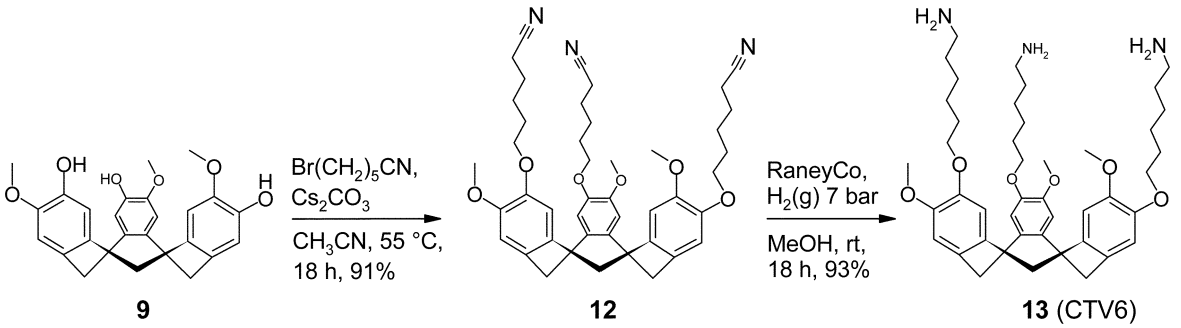
C-Pivot based multicoordinate ligands. In contrast to the previously mentioned trityl and CTV platforms the structure of the C_3-symmetric C-pivot platform **3** is relatively simple (Chart 1). The synthesized C-pivot platform **20** consists of a central C-atom on which a *tert*-butylphenyl group is connected and three CMPO ligating groups connected by $-(CH_2)_3-$ spacers. The C-pivot platform **17** was prepared in three steps, starting from the commercially available tris-(2-cyanoethyl)nitromethane, as described in the literature.[17] Reaction of the free amine in **17** with 4-*tert*-butylbenzoyl chloride gave the C-pivot **18** in 47% yield. Deprotection of the BOC groups in **18** with TFA afforded the TFA salt of C-pivot **19**. This salt was subsequently reacted with the *p*-nitrophenol activated ester of CMPO to give the required pivCMPO ligand **20** in 59% yield (Scheme 5).

Extraction results

Ideally the organic solvent for actinide solvent extraction processes should be stable, have a low water-miscibility, a



Scheme 3

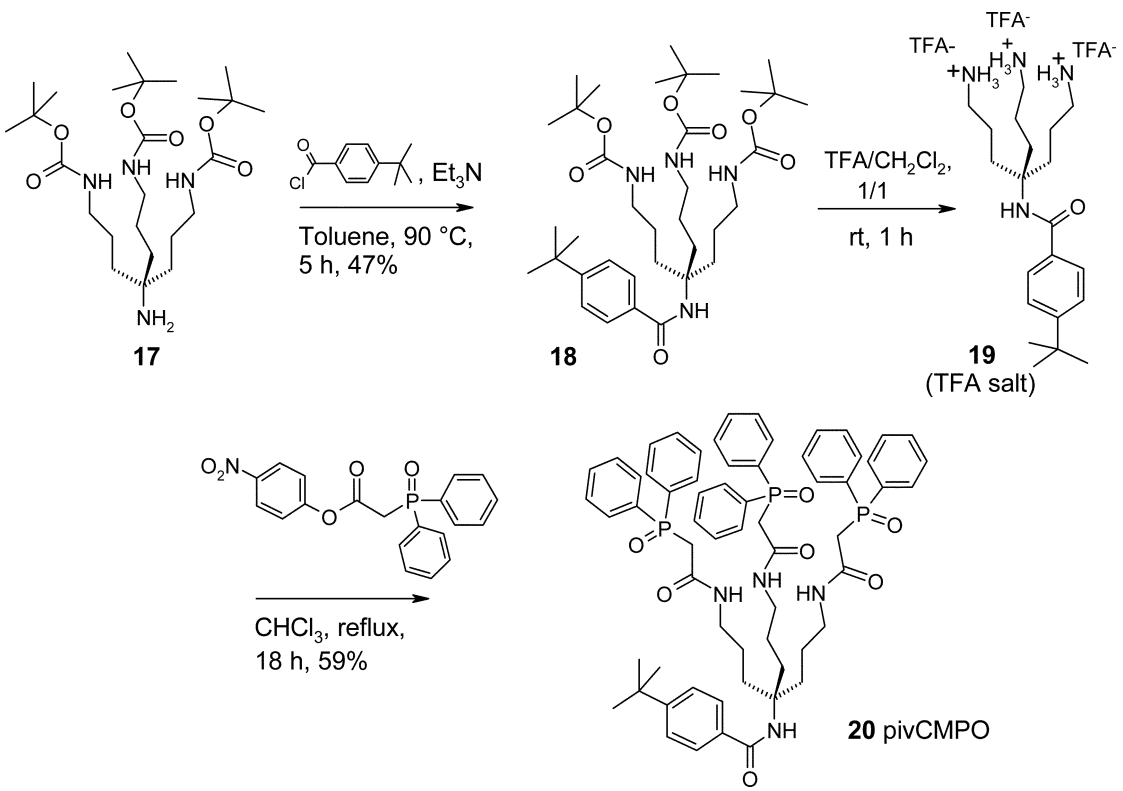


Scheme 4

relatively low vapor pressure, and no significant harmful effects on the environment.[18,19] The extraction efficiency of ligands is directly related to the solubility of the ligand–metal complex in the organic phase. Strongly coordinating polar solvents dissolve metal complexes generally better. This results normally in significantly higher D_{Am} values, whereas the $S_{Am/Eu}$ values are less easily affected by changing the solvent. The effects of several solvents on the extraction efficiency of Am^{3+} and Eu^{3+} using **7**–tritCMPO and **16**–CTV6CMPO were examined (Table 1).

Table 1 shows that there is a wide variety in the D_{Am} values (0.1–30), whereas the $S_{Am/Eu}$ values stay between 0.8–1.7. Nitrobenzene, the most polar solvent of this series, gives the highest extraction efficiency for **16**–CTV6CMPO. Despite that *n*-octanol is rather apolar, the D_{Am} values for the ligands measured in this solvent are also relatively high. This can be explained by the ability of *n*-octanol to form hydrogen bonds and having a strongly coordinating oxygen atom. Since nitrobenzene[20] gave satisfactory extraction results, and all prepared ligands could be dissolved in it, this solvent was chosen as the organic phase in the extraction experiments.

Extraction properties of the CTV, trityl, and C-pivot based ligands. The extraction data of the CTV based multicoordinate ligands are summarized in Table 2. The CTV platform is very rigid, ligating groups directly connected to it (Chart 2) are rather constricted in their movements. Due to a rigid preorganization of the ligating groups the ΔS of complex formation will be less negative which is advantageous for the extraction process. A rigid conformation leaves, however, little room for rearrangement of the ligating groups. The latter is probably the origin of the very low extraction efficiencies of the CTV0 ligands. However, a large increase of the extraction efficiency is observed upon elongation of the $-(CH_2)_n-$ spacer to $n = 3$ and 6. For lower rim CMPO-functionalized calix[4]arenes a similar increase in extraction on elongation of the $-(CH_2)_n-$



Scheme 5

Table 1 D_{Am} and $S_{Am/Eu}$ values of ligands **7**–tritCMPO and **16**–CTV6CMPO (c_L = 10^{-3} M, 3 M HNO_3) in six different solvents[18,19]

Solvent	Dipole moment/ C m	Dielectric constant	TritylCMPO		CTV6CMPO	
			D_{Am}	$S_{Am/Eu}$	D_{Am}	$S_{Am/Eu}$
Nitrobenzene[a]	4.22	34.78	2.8	1.3	30	1.3
Dichloroethane	1.83	10.36	5.3	1.6	5.8	1.6
n-Octanol	1.76	10.34	21	1.1	23	1.2
Tetrachloroethane	1.30	8.20	8.1	0.8	4.6	1
Dichloromethane	1.14	8.93	2.5	1.5	2.7	1.5
Chloroform	1.15	4.89	1.2	1.3	0.1	1.7

[a] c_L = 10^{-4} M.

spacer has been observed.[21] The increased 'mobility' of the ligating groups allows for a more optimal bond geometry and hence the formation of stronger ligand–metal cation bonds. From the log *D vs.* log [*L*] curves of the CTV–CMPO ligands (Fig. 1 and 2; *vide infra*) it can be concluded that CTV6CMPO is significantly more and CTV0CMPO significantly less efficient in extracting Am^{3+} as compared to the other ligands, stressing the influence of the $-(CH_2)_n-$ spacer. From Tables 2 and 3 the following order of Am^{3+} extraction efficiencies can be observed for the CMPO ligands: CTV6CMPO > tritCMPO ≈ pivCMPO > CTV3CMPO > CTV0CMPO. The ligands have comparable $S_{Am/Eu}$ values, ranging from 1.4 to 1.8. The platform is thus mostly influencing the extraction efficiencies.

In contrast to the CMPO derivatives all DGA derivatives have selectivities for Eu^{3+} over Am^{3+} up to a $S_{Eu/Am}$ of 5, which is known for DGA multicoordinate ligands.[22] Surprisingly, the CTV3- and CTV6PICO ligands also have selectivity for Eu^{3+}. The calix[*n*]arene-PICO ligands studied by Casnati *et al.* have $S_{Am/Eu}$ values ranging from 2 to 14 at the same HNO_3 concentration.[23] The three MPMA multicoordinate ligands based on the CTV scaffold have selectivity for Eu^{3+} at 0.001 M HNO_3. Comparison of these extraction results with those of tritylMPMA in Table 2 shows that changing the platform from CTV to trityl results in a change in the Am^{3+} selectivity of the MPMA derivatives at 0.001 M HNO_3. Significant differences in the Am/Eu selectivity can thus be obtained by simply changing the platform. At higher acidities the CTV-MPMA ligands do not extract Am^{3+} and Eu^{3+} any more (Table 4), whereas the tritylMPMA does extract at 3 M HNO_3. The tritylMPMA ligand is a more efficient extractant than its CTV analogues, therefore its competition with protonation is stronger resulting in an observable extraction at 3 M HNO_3.

Stoichiometry of complexation. The complexation stoichiometries of the complexes of the CMPO ligands were deduced using the following method.

The general extraction equilibrium in solution can be expressed as eqn (1), where a solid line denotes the species in the organic phase: [24]

$$M^{x+} + xNO_3^- + nL \rightleftharpoons \overline{ML_n(NO_3)_x} \qquad (1)$$

Table 2 D_{Am} and $S_{Am/Eu}$ values of the ligands based on the CTV0, CTV3, and CTV6 platforms, c_L = 10^{-2} M at 0.001 and 3 M HNO_3

	Ligand	HNO_3		Ligand	HNO_3	
		10^{-3} M	3 M		10^{-3} M	3 M
D_{Am}	CTV0CMPO	1.26	0.08	CTV0PICO	nd	nd
D_{Eu}		0.89	0.05		nd	nd
$S_{Am/Eu}$		1.4	1.6			
D_{Am}	CTV3CMPO	>40	2.95	CTV3PICO	<0.02	<0.01
D_{Eu}		>40	1.95		0.07	<0.01
$S_{Am/Eu}$			1.5		<0.3	
D_{Am}	CTV6CMPO[b]	59	1.38	CTV6PICO	0.37	<0.01
D_{Eu}		36	1.02		0.53	<0.01
$S_{Am/Eu}$		1.6	1.4		0.7	
D_{Am}	CTV0DGA	nd[a]	nd[a]	CTV0MPMA	0.09	<0.01
D_{Eu}		nd[a]	nd[a]		0.34	<0.01
$S_{Am/Eu}$					0.3	
D_{Am}	CTV3DGA	4.8	0.15	CTV3MPMA	0.28	<0.01
D_{Eu}		7.0	0.72		0.69	<0.01
$S_{Am/Eu}$		0.7	0.21		0.4	
D_{Am}	CTV6DGA	21.4	0.75	CTV6MPMA	0.76	<0.01
D_{Eu}		>40	3.5		2.12	<0.01
$S_{Am/Eu}$		<0.5	0.21		0.4	

[a] nd (not determined). Major precipitation. [b] [L] = 10^{-5} M.

The extraction equilibrium constant depends on the concentrations of the species in solution expressed as eqn (2).

$$K_{ex} = \frac{\overline{[ML_n(NO_3)_x]}}{[M^{x+}][NO_3^-]^x[L]^n} \qquad (2)$$

The distribution ratio *D* is defined as the ratio of the total amount of metal extracted in the organic layer and the total amount in the aqueous layer (eqn (3)).

$$D_M = \frac{\overline{[ML_n(NO_3)_x]}}{[M^{x+}]} \qquad (3)$$

Eqn (3) can also be written as eqn (4).

$$\log D_M = \log(K_{ex}[NO_3^-]^x) + n\log[\bar{L}] \qquad (4)$$

According to eqn (4) there is a linear relationship between the logarithmic function of *D* and the logarithmic function of the ligand concentration. The slope of the resulting plot should be equal to the number of ligand molecules per metal cation in the extracted species. The "free" CMPO ligand has a metal to ligand stoichiometry of 1 : 3.[5] Therefore, a stoichiometry of 1 : 1 can be assumed for multicoordinating ligands having three CMPO groups. However, due to several factors, like changes in the flexibility or steric environment of the ligating groups different stoichiometries may be obtained. The log D_M *vs.* log [L] graphs of the ligands CTV0CMPO, CTV3CMPO, and CTV6CMPO are shown in Fig. 1 and that of tritCMPO and pivCMPO in Fig. 2. CTV6CMPO and CTV3CMPO have similar slopes of 1.3, the closest stoichiometry being a 4 : 5 metal to ligand ratio. The complexes could thus be oligomeric in nature; however, the values of the slopes give the approximate overall composition of the extracted species. Whether the species is a single complex, oligomeric, or polymeric cannot be deduced from these experiments. In principle, the

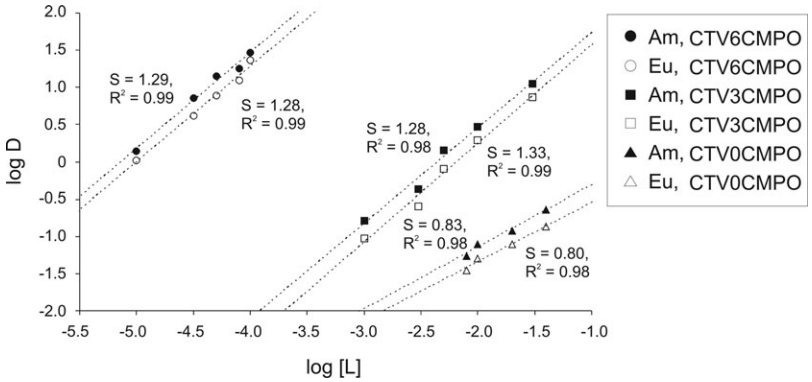


Fig. 1 Plots of log D_{Am} *vs.* log [*L*] at 3 M HNO_3.

complexes could thus also exist as a mixture of 1 : 1 and 2 : 3 metal to ligand species. The slope of the log *D* *vs.* log [L] line of CTV0MPO is 0.8, which indicates a reversed stoichiometry of a 5 : 4 metal to ligand ratio with regard to the previous two ligands. Complexes are formed in which the ligands bind on average to more than one metal. These observations seem peculiar since the latter is unlikely for rigid ligands such as CTV0CMPO and the metal to ligand ratio of more than 1 is unexpected for the more flexible CTV3CMPO and CTV6CMPO ligands. It should, however, be kept in mind that complexes with a saddle geometry are in principle possible.[11] This geometry allows a 'more than one metal bonding' for the CTV0CMPO ligand.

The corresponding slopes of pivCMPO are 1.5, suggesting a 2 : 3 metal to ligand stoichiometry for the complexes. For tritCMPO the slope is not linear over the whole concentration range. The line starts with a slope of about 0.7, indicating a 3 : 2 metal to ligand stoichiometry, at approximately [L] = 3×10^{-4} M. Than a region can be recognized where the slope is zero, which means that the distribution ratio is independent of the ligand concentration. Here most probably a structural reorganization of the extracted species takes place which is completed at [L] $\approx 2 \times 10^{-3}$ M where the slope becomes 0.7 again. For all the CMPO derivatives the stoichiometries of their Am^{3+} as compared to their Eu^{3+} complexes are the same.

Effect of nitric acid on the extraction. The effect of the HNO_3 concentration in the aqueous phase on the extraction behavior was studied for tritCMPO, pivCMPO, and all CTV6 derivatives (Table 4). The extraction efficiencies are influenced by a combined HNO_3 salting out effect and protonation of the ligand, dependent on its basicity. The extraction behavior of CTV6DGA is irregular upon changing the acidity. The maximum at 0.001 M HNO_3 is decreasing to a minimum between 0.1–1 M HNO_3 followed by a maximum at 3 M HNO_3, whereupon it decreases again as a result of the opposing effects previously mentioned. For both the PICO and MPMA derivatives a fast decrease in extraction is observed; at 0.1 M HNO_3 there is no significant metal extraction any more. For PICO derivatives this is understandable considering the easily protonated pyridine nitrogen atom. Malonamides preorganized on a tripodal C-pivot, having a $-(CH_2O(CH_2)_3)-$ spacer, or trialkylbenzene platforms have a small selectivity towards Am^{3+} with regard to Eu^{3+} and have an increase in extraction efficiency ongoing from 1 to 3 M HNO_3.[25,26] The combined effects of the protonation of the ligating groups and the differences in preorganization of the CTV6 platform may be the reason for the opposite extraction behavior of the CTV6MPMA ligand.

The phosphoryl oxygen in CMPO extractants is protonated under the conditions of nuclear waste treatment (~3 M HNO_3).[27,28] The extraction efficiency of this type of ligand

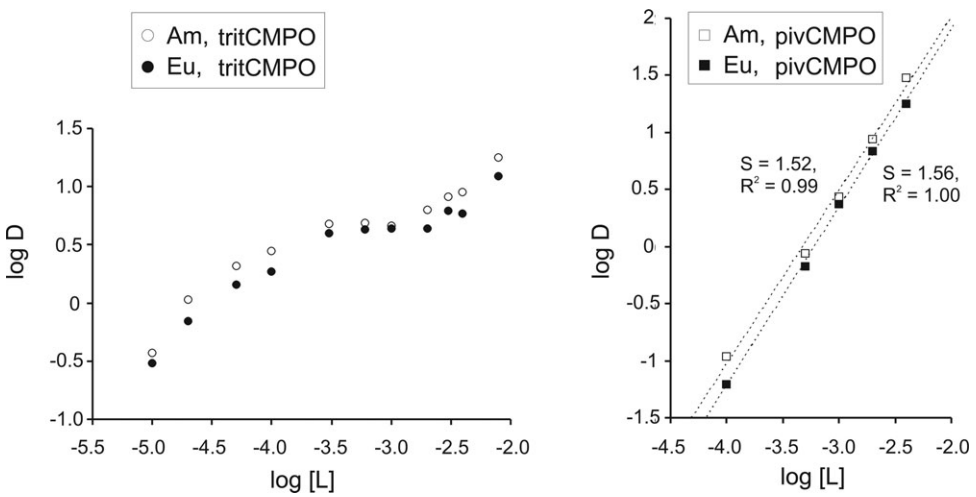


Fig. 2 Plots of log D_{Am} *vs.* log [*L*] at 3 M HNO_3.

Table 3 D_{Am} and $S_{Am/Eu}$ values of the ligands based on the trityl and C-pivot platforms at 0.001 and 3 M HNO_3

		HNO_3			HNO_3			HNO_3	
	Ligand[a]	10^{-3} M	3 M	Ligand[b]	10^{-3} M	3 M	Ligand[a]	10^{-3} M	3 M
D_{Am}	TritylCMPO	10.7	2.8	TritylPICO	>100	<0.01[c]	pivCMPO	63	0.11
D_{Eu}		6.25	1.8		>100	<0.01[c]		41	0.06
$S_{Am/Eu}$		1.7	1.6					1.5	1.8
D_{Am}	TritylDGA	>100	13.2	TritylMPMA	5.8	1.35			
D_{Eu}		>100	36		3.68	5.97			
$S_{Am/Eu}$			0.4		1.6	0.2			

[a] [L] = 10^{-4} M. [b] [L] = 10^{-1} M. [c] Major precipitation.

largely depends on the basicity of the carbonyl and phosphoryl oxygens and is regulated by their substituents. The platform also influences the behavior of the multicoordinate ligand towards the HNO_3 concentration.[4] From Table 4 it can be seen that CTV6CMPO gives a regular decrease in extraction efficiency from 0.001 M to 6 M HNO_3. A similar, though somewhat faster decrease in extraction efficiency is observed for the pivCMPO ligand. TritCMPO exhibits a totally different behavior; there is a maximum extraction observed at 0.01 M HNO_3 and a minimum at around 1 M HNO_3 from which it goes up again. In contrast, when the trityl is preorganized with CMPO groups at the 'opposite' side of the molecule it results in a strong decrease in extraction upon increasing the HNO_3 concentration.[29] The origin of these differences in extraction behavior is not known in detail. However, it is probably related to an interplay of the salting out effect and the protonation of the ligating groups, which determines the competitive behavior of the multicoordinate ligand between the protons and metal ions. For most ligands the $S_{Am/Eu}$ values change only slightly, except for the CTV6DGA and CTV6PICO ligand. For the former ligand the selectivity for Eu^{3+} is almost tripled, going from 0.01 M to 3 M HNO_3 and for the latter it is reversed from 0.001 M to 0.01 M HNO_3. It is unlikely that this behavior is originating from changes in the aqueous phase, since it is not observed for the other ligands.

Conclusions

Three different platforms, of which one platform has three different $-(CH_2)_n-$ spacer lengths, were successfully synthesized and functionalized with Am^{3+} ligating groups resulting in fifteen new ligands. The extraction efficiencies of these multicoordinate ligands are largely governed by the properties of the platform. Their $S_{Am/Eu}$ values range between 0.2 and 2.0 and are, for the non CMPO ligands, largely dependent on the HNO_3 concentration. The D_{Am} values differ much more and follow the order CTV6 > trityl ≈ C-pivot > CTV3 > CTV0 with a maximum for CTV6CMPO of D_{Am} = 30 ($S_{Am/Eu}$ = 1.4, c_L = 10^{-4} M, 3 M HNO_3). The rigid preorganization of ligating groups on the CTV0 platform did not result in increased $S_{Am/Eu}$ values. The CMPO derivatives have

Table 4 D_{Am} and $S_{Am/Eu}$ values from ligands tritCMPO, pivCMPO, and the CTV6 based ligands at varying HNO_3 concentrations

			[HNO_3]/M							
Ligand	[L]/M		0.001	0.003	0.01	0.03	0.1	1	3	6
tritCMPO	10^{-4}	D_{Am}	12.0	13.2	18.6	3.24	0.62	0.27	2.82	13.2
		D_{Eu}	7.76	8.71	9.12	2.04	0.38	0.16	1.82	9.55
		$S_{Am/Eu}$	1.5	1.5	2.0	1.6	1.6	1.7	1.5	1.4
pivCMPO	10^{-4}	D_{Am}	63.1	31.6	13.2	9.12	1.58	0.13	0.11	0.04
		D_{Eu}	40.7	21.4	11.2	7.59	1.12	0.08	0.06	0.03
		$S_{Am/Eu}$	1.6	1.5	1.2	1.2	1.4	1.6	1.8	1.3
CTV6CMPO	10^{-5}	D_{Am}	58.9	nd[a]	20.4	nd[a]	5.75	1.55	1.38	0.06
		D_{Eu}	36.3	nd[a]	15.5	nd[a]	3.80	1.05	1.02	0.05
		$S_{Am/Eu}$	1.6	nd[a]	1.3	nd[a]	1.5	1.5	1.4	nd
CTV6DGA	10^{-2}	D_{Am}	21.4	nd	5.73	nd	<0.01	<0.01	0.75	0.14
		D_{Eu}	>40	nd	9.11	nd	<0.01	<0.01	3.5	0.73
		$S_{Am/Eu}$	<0.5	nd	0.6	nd	nd	nd	0.2	0.2
CTV6PICO	10^{-2}	D_{Am}	0.37	nd	0.20	nd	<0.02	<0.02	<0.01	<0.01
		D_{Eu}	0.53	nd	0.17	nd	<0.02	<0.02	<0.01	<0.01
		$S_{Am/Eu}$	0.7	nd	1.2	nd	nd	nd	nd	nd
CTV6MPMA	10^{-2}	D_{Am}	0.76	nd	0.04	nd	<0.02	<0.02	<0.01	<0.01
		D_{Eu}	2.12	nd	0.11	nd	<0.02	<0.02	<0.01	<0.01
		$S_{Am/Eu}$	0.4	nd	0.4	nd	nd	nd	nd	nd

[a] nd (not determined).

comparable $S_{Am/Eu}$ values, ranging from 1.4 to 1.8, and so the platform is thus mostly influencing the extraction efficiencies. The threefold preorganization of platforms with CMPO groups[5] did not result in improved extraction properties. The observed extraction results are comparable to that of CMPO-functionalized cavitands[6b] and lower rim CMPO-functionalized calix[4]arenes.[30] Only the upper rim CMPO-functionalized calix[4]arenes in which the CMPO groups are directly connected to the phenyl rings (similar to CTV0CMPO) have a significant higher extraction efficiency and selectivity for Am^{3+}.[31] These superior extraction properties thus most likely result from a combination of the electronic effect of the phenyl substituents and a preferential preorganization of the CMPO groups by the calix[4]arene.

The extraction efficiencies of the multicoordinate ligands with the DGA, MPMA, and PICO ligating groups are lower than that of the CMPO analogues. All the multicoordinate ligands based on the DGA ligating groups have a selectivity for Eu^{3+} up to $S_{Eu/Am} = 5$. These values are comparable to those published for a DGA-functionalized trityl.[22]

The results also show that protonation of the ligands has significant influences on their extraction behavior. $S_{Am/Eu}$ values can reverse, for instance for CTV6PICO from $S_{Am/Eu} = 0.7$ at 0.001 M HNO_3 to 1.2 at 0.01 M HNO_3. The D_{Am} values change significantly for all ligands upon a change in the HNO_3 concentration.

Experimental

General information and instrumentation

All moisture-sensitive reactions were carried out under an argon atmosphere. The solvents and all reagents were obtained from commercial sources and used without further purification. Solvents were dried according to standard procedures and stored over molecular sieves. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unity INOVA (300 MHz) spectrometer. ^{1}H NMR chemical shift values (300 MHz) are reported as δ using the residual solvent signal as an internal standard ($CDCl_3$, δ 7.257). ^{13}C NMR chemical shift values (75 MHz) are reported as δ using the residual solvent signal as an internal standard ($CDCl_3$, δ 77.0). Fast atom bombardment (FAB) mass spectra were recorded with a Finnigan MAT 90 spectrometer. Matrix-assisted laser desorption ionization (MALDI) TOF mass spectra were recorded using a Perkin Elmer/PerSpective Biosystems Voyager-DE-RP MALDI-TOF mass spectrometer. Elemental analyses were performed using a Carlo Erba EA1106 instrument. Analytical TLC was performed using Merck prepared plates (silica gel 60 F-254 on aluminium). Merck silica gel (40–63 μm) was used for flash chromatography. Column chromatography was carried out on Merck silica gel 60 (230–400 mesh). Compounds **4** and **5**,[10] the activated esters of CMPO,[32] DGA,[33] PICO,[23] and MPMA[9] were synthesized according to literature procedures.

Syntheses

Tris(3,5-di-*tert*-butyl-2-aminoethoxyphenyl)methane (6). A solution of trityl **5** (15.0 g, 20.1 mmol) and BH_3 (121 mL, 1 M solution in THF) was refluxed in dry THF (500 mL total) for 16 h. Concentrated HCl (25 mL) was added and the mixture was refluxed for 30 min. The mixture was basified with NaOH (aq) to pH ~10. Most of the solvent was evaporated under reduced pressure and the crude product was taken up into CH_2Cl_2 (200 mL). The aqueous layer was washed with CH_2Cl_2 (3 × 50 mL) and dried with $MgSO_4$. Evaporation of the solvent afforded 17.8 g of a white powder, which was purified by recrystallization from MeOH giving **6** as white crystals. Yield 14.5 g (95%); mp 155–157 °C. The results of the analytical analysis (^{1}H NMR, ^{13}C NMR, and mass spectrometry) corresponded with the data described in literature.[10]

Tris(3,5-di-*tert*-butyl-2-(((*N*,*N*-dimethyl-3-oxapentanamide)-amino)ethoxy)phenyl)methane (7–tritDGA). A solution of trityl **6** (0.40 g, 0.53 mmol) and the *p*-nitrophenol activated ester of DGA (0.46 g, 1.64 mmol) in $CHCl_3$ (30 mL) was refluxed for 2 d. The solvent was evaporated under reduced pressure and the crude product was taken up into CH_2Cl_2 (30 mL). The organic layer was washed with 1 M NaOH (7 × 20 mL) and H_2O (20 mL) and dried with $MgSO_4$. Evaporation of the solvent afforded 0.52 g of the crude product as a yellowish powder. Trituration with Et_2O gave **7**–tritDGA as a white solid. Yield 0.39 g (50%); mp 158 °C; FAB-MS: *m*/*z* 1188.0 ($[M + H]^+$, calc. 1187.8); ^{1}H NMR δ: 7.90 (t, 3H, J = 6.0 Hz, NH), 7.30 (d, 3H, J = 2.1 Hz, PhH), 7.19 (d, 3H, J = 2.4 Hz, PhH), 6.52 (s, 1H, CH), 4.32 (s, 6H, $OCH_2C(O)$), 4.12 (s, 6H, $OCH_2C(O)$), 3.78 (br t, 6H, OCH_2), 3.54 (br t, 6H, CH_2NHO), 2.99 (s, 9H, CH_3), 2.97 (s, 9H, CH_3), 1.36 (s, 27H, $C(CH_3)_3$), 1.23 (s, 27H, $C(CH_3)_3$); ^{13}C NMR δ: 170.1, 169.0, 153.0, 144.9, 141.9, 137.3, 127.0, 122.5, 71.2, 70.5, 69.8, 39.7, 37.7, 36.0, 35.6, 35.5, 34.5, 31.5, 31.4. Anal. Calc. for $C_{67}H_{106}N_6O_{12}$: C, 67.76; H, 9.00; N, 7.08. Found: C, 67.69; H, 8.91; N, 6.99%.

Tris(3,5-di-*tert*-butyl-2-(((pyridine-2-carbonyl)amino)ethoxy)-phenyl)methane (7–tritPICO). A solution of trityl **6** (0.50 g, 0.66 mmol) and picolinic acid pentafluorophenyl ester (0.59 g, 2.04 mmol) in $CHCl_3$ (30 mL) was refluxed for 2 d. The solvent was evaporated under reduced pressure and the crude product was taken up into CH_2Cl_2 (30 mL). The organic layer was washed with 1 M NaOH (7 × 20 mL) and H_2O (20 mL) and dried with $MgSO_4$. Evaporation of the solvent afforded 0.64 g of the crude product which was subjected to column chromatography (SiO_2, eluent EtOAc) giving **7**–tritPICO as a white powder. Yield 0.56 g (80%); mp 85–86 °C; FAB-MS: *m*/*z* 1073.6 ($[M + H]^+$, calc. 1073.7); ^{1}H NMR δ: 8.55 (d, 3H, J = 5.7 Hz, PhH), 8.12 (d, 3H, J = 4.5 Hz, PhH), 7.72 (t, 3H, J = 9.6 Hz, PhH), 7.39 (t, 3H, J = 9.6 Hz, PhH), 7.29–7.34 (m, 3H, PhH), 7.19 (d, 3H, J = 1.4 Hz, PhH), 6.65 (s, 1H, CH), 3.86–3.92 (m, 6H, OCH_2), 3.60 (t, 6H, J = 5.1 Hz, CH_2NHO), 1.30 (s, 27H, $C(CH_3)_3$), 1.23 (s, 27H, $C(CH_3)_3$); ^{13}C NMR δ: 164.2, 153.0, 149.8, 147.9, 144.9, 142.1, 137.4, 127.1, 125.9, 122.6, 122.1, 70.7, 39.9, 37.7, 35.5, 34.5, 31.5, 31.3. Anal. Calc. for $C_{67}H_{88}N_6O_6 \cdot 0.25CH_2Cl_2$: C, 73.83; H, 8.15; N, 7.68. Found: C, 73.82; H, 8.10; N, 7.62%.

Tris(3,5-di-*tert*-butyl-2-((*N*-phenyl-*N*-methylmalonamido)-ethoxy)phenyl)methane (7–tritMPMA). A solution of trityl **6** (0.50 g, 0.66 mmol), *N*-phenyl-*N*-methylmalonic acid (0.42 g, 2.2 mmol), and DCC (0.41 g, 2.0 mmol) in THF (40 mL) was

stirred for 3 d at rt. The suspension was cooled to −18 °C and the white precipitate was filtered off. The filtrate was evaporated under reduced pressure and the crude product was taken up into Et_2O (50 mL). The organic layer was washed with $NaHCO_3$ (3 × 20 mL) and H_2O (2 × 20 mL) and dried with $MgSO_4$. Evaporation of the solvent afforded 0.84 g of the crude product as a white foam. This was subjected to column chromatography (SiO_2, eluent EtOAc) to give **7**–tritMPMA as a white solid. Yield 0.45 g (83%); mp 172–173 °C; FAB-MS: *m*/*z* 1283.9 ($[M + H]^+$, calc. 1283.8); ^{1}H NMR *δ*: 8.26 (s, 3H, NH), 7.30–7.42 (m, 10H, PhH), 7.22–7.24 (m, 8H, PhH), 7.15 (d, 3H, *J* = 2.1 Hz, PhH), 6.42 (s, 1H, CH), 3.64 (br t, 6H, OCH_2), 3.48 (br t, 6H, CH_2NHO), 3.28 (s, 9H, CH_3), 3.17 (s, 6H, CH_3), 1.28 (s, 27H, $C(CH_3)_3$), 1.18 (s, 27H, $C(CH_3)_3$); ^{13}C NMR *δ*: 168.1, 167.3, 153.0, 144.8, 143.2, 141.9, 137.3, 130.0, 128.2, 127.1, 127.0, 122.5, 70.5, 40.5, 40.2, 37.9, 37.6, 35.4, 34.5, 31.4, 31.4. Anal. Calc. for $C_{79}H_{106}N_6O_9$: C, 73.81; H, 8.32; N, 6.55. Found: C, 73.79; H, 8.41; N, 6.49%.

2,7,12-Trimethoxy-3,8,13-tris(*N*-Boc-aminopropoxy)-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (10). A suspension of **9** (0.50 g, 1.22 mmol), *tert*-butyl-*N*-(3-bromopropyl)carbamate (1.17 g, 4.9 mmol), and Cs_2CO_3 (2.39 g, 7.34 mmol) was stirred in CH_3CN (50 mL) for 18 h at 55 °C. The solvent was removed under reduced pressure and the residue was taken up in $CHCl_3$ (50 mL). The precipitate was filtered off over hyflo gel and the solvent was removed under reduced pressure. Trituration of the crude product with hexane–diisopropyl ether and drying *in vacuo* gave **10** as a white powder. Yield 0.93 g (86%); mp 136–139 °C; MALDI-TOF-MS: *m*/*z* 879.7 ($[M]^+$, calc. 879.5); ^{1}H NMR *δ*: 6.83 (s, 3H, ArH), 6.81 (s, 3H, ArH), 5.38 (s, 3H, NH), 4.75 (d, 3H, *J* = 13.9 Hz, ArC*H*HAr), 4.06–4.13 (m, 3H, ArOC*H*H), 3.94–4.01 (m, 3H, ArOCH*H*), 3.83 (s, 9H, $ArOCH_3$), 3.53 (d, 3H, *J* = 13.9 Hz, ArC*H*HAr), 3.30–3.32 (m, 6H, CH_2NH), 1.96 (m, 6H, CH_2), 1.43 (s, 27H, CH_3); ^{13}C NMR *δ*: 156.1, 148.4, 147.0, 132.6, 131.7, 115.5, 113.5, 78.9, 68.5, 56.1, 38.8, 36.5, 29.4, 28.5. Anal. Calc. for $C_{48}H_{69}N_3O_{12}$: C, 65.51; H, 7.90; N, 4.77. Found: C, 65.53; H, 7.84; N, 4.74%.

2,7,12-Trimethoxy-3,8,13-tris(ammoniopropoxy)-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (11a–CTV3). A solution of **10** (0.93 g, 1.06 mmol) and TFA (12 mL) in CH_2Cl_2 (12 mL) was stirred for 3 h at rt, after which it was quenched by the addition of Et_2O (20 mL). The precipitate was filtered off, washed extensively with Et_2O and dried *in vacuo* to afford **11a**–CTV3 as a white solid. Yield 0.94 g (97%); HRM, FAB-MS: *m*/*z* 919.851 ([M–2H$^+$], calc. 919.820); ^{1}H NMR *δ*: (CD_3OD) 7.08 (s, 3H, ArH), 7.05 (s, 3H, ArH), 4.73–4.83 (m, 3H, ArC*H*HAr), 4.07–4.23 (m, 6H, $ArOCH_2$), 3.84 (s, 9H, $ArOCH_3$), 3.59 (d, 3H, *J* = 13.9 Hz, ArC*H*HAr), 3.18 (t, 6H, *J* = 6.6 Hz, CH_2N), 2.11 (q, 6H, *J* = 6.0 Hz, CH_2); ^{13}C NMR *δ*: (CD_3OD) 149.5, 147.6, 135.1, 133.9, 117.4, 114.9, 69.6, 56.7, 39.7, 36.8, 28.0.

2,7,12-Trimethoxy-3,8,13-tris(nitrilohexyloxy)-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (12). A suspension of **9** (1.04 g, 2.54 mmol), 6-bromohexanenitrile (2.68 g, 15.2 mmol), and Cs_2CO_3 (4.96 g, 15.2 mmol) in CH_3CN (50 mL) was stirred at 55 °C for 18 h. The solvent was removed under reduced pressure and the residue was taken up in CH_2Cl_2 (50 mL). The organic layer was washed with H_2O (3 × 30 mL), 1 M HCl (3 × 10 mL), and dried with $MgSO_4$. The solvent was removed under reduced pressure. Trituration (Et_2O) gave **12** as a white solid. Yield 1.60 g (91%); mp 113–117 °C; MALDI-TOF-MS: *m*/*z* 693.8 ($[M + H]^+$, calc. 693.4); ^{1}H NMR *δ*: 6.83 (s, 3H, ArH), 6.82 (s, 3H, ArH), 4.75 (d, 3H, *J* = 13.9 Hz, ArC*H*HAr), 3.91–4.06 (m, 6H, $ArOCH_2$), 3.82 (s, 9H, $ArOCH_3$), 3.53 (d, 3H, *J* = 13.9 Hz, ArC*H*HAr), 2.35 (t, 6H, *J* = 7.0 Hz, CH_2CN), 1.82 (q, 6H, *J* = 6.8 Hz, $ArOCH_2CH_2$), 1.59–1.75 (m, 12H, CH_2CH_2); ^{13}C NMR *δ*: 148.4, 147.2, 132.4, 132.0, 119.6, 115.7, 114.1, 69.0, 56.4, 36.5, 28.5, 25.4, 25.2, 17.1. Anal. Calc. for $C_{42}H_{51}N_3O_6$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.74; H, 7.49; N, 6.09%.

2,7,12-Trimethoxy-3,8,13-tris(aminohexyloxy)-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (13–CTV6). To a suspension of **11** (0.51 g, 0.73 mmol) in MeOH (30 mL) was added a small quantity of NH_3 and RaneyCo. The mixture was hydrogenated under 7 bar H_2 in an autoclave at rt for 18 h. The active hydrogen was removed from the catalyst by flushing with argon and the solvent was removed under reduced pressure. The crude product was taken up in $CHCl_3$ (50 mL) and the mixture was filtered over hyflo and dried with $MgSO_4$. Removing of the solvent afforded **13**–CTV6. Yield 0.48 g (93%); mp 111–113 °C; MALDI-TOF-MS: *m*/*z* 707.2 ($[M + 2H]^+$, calc. 707.5); ^{1}H NMR *δ*: 6.83 (s, 3H, ArH), 6.81 (s, 3H, ArH), 4.73 (d, 3H, *J* = 13.6 Hz, ArC*H*HAr), 3.89–4.04 (m, 6H, $ArOCH_2$), 3.81 (s, 9H, $ArOCH_3$), 3.52 (d, 3H, *J* = 13.9 Hz, ArC*H*HAr), 2.67 (t, 6H, *J* = 6.6 Hz, CH_2NH_2), 1.79 (q, 6H, *J* = 7.0 Hz, $ArOCH_2CH_2$), 1.33–1.52 (m, 18H, $CH_2CH_2CH_2$); ^{13}C NMR *δ*: (CD_3OD) 149.5, 148.5, 134.3, 134.2, 116.9, 115.5, 70.5, 57.1, 42.0, 37.0, 31.8, 30.5, 27.8, 27.1. Anal. Calc. for $C_{42}H_{63}N_3O_6$: C, 71.46; H, 8.99; N, 5.95. Found: C, 71.49; H, 8.97; N, 5.93%.

2,7,12-Trimethoxy-3,8,13-tris((diphenylphosphoryl)acetamido)-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (14–CTV0CMPO). A suspension of **8** (0.15 g, 0.37 mmol) and the *p*-nitrophenyl activated ester of CMPO (0.47 g, 1.22 mmol) in toluene (20 mL) was refluxed for 18 h. The solvent was evaporated under reduced pressure and the crude product was taken up into $CHCl_3$ (20 mL). The organic layer was washed with 1 M NaOH (3 × 20 mL) and H_2O (20 mL) and dried with Na_2SO_4. Removal of the solvent, followed by column chromatography (SiO_2, eluent 7.5% EtOH in CH_2Cl_2) afforded **14**–CTV0CMPO. Yield 0.31 g (73%); mp 164–167 °C; MALDI-TOF-MS: *m*/*z* 1132.9 ($[M + H]^+$, calc. 1132.4); ^{1}H NMR *δ*: 9.30 (s, 3H, NH), 8.25 (s, 3H, ArH), 7.68–7.80 (m, 12H, PhH), 7.39–7.57 (m, 18H, PhH), 6.84 (s, 3H, ArH), 4.68 (d, 3H, *J* = 13.6 Hz, ArC*H*HAr), 3.80 (s, 9H, $ArOCH_3$), 3.54 (d, 3H, *J* = 13.2 Hz, ArC*H*HAr), 3.44 (d, 3H, *J* = 12.8 Hz, COC*H*HP), 3.43 (d, 3H, *J* = 12.8 Hz, COCH*H*P); ^{13}C NMR *δ*: 162.4, 162.3, 147.4, 135.3, 132.3, 131.0, 130.8, 130.7, 128.9, 128.7, 126.2, 121.1, 111.7, 56.1, 40.8, 40.0, 36.3. Anal. Calc. for $C_{66}H_{60}N_3O_9P_3$: C, 70.02; H, 5.34; N, 3.71. Found: C, 70.33; H, 5.36; N, 3.78%.

2,7,12-Trimethoxy-3,8,13-tris(*N*,*N*-dimethyl-3-oxaglutaramido)-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (14–CTV0DGA). A suspension of **8** (0.13 g, 0.31 mmol) and the *p*-nitrophenol ester

of DGA (0.49 g, 1.85 mmol) in toluene (15 mL) was refluxed for 18 h. The solvent was evaporated under reduced pressure and the crude product was taken up into $CHCl_3$ (20 mL). The organic layer was washed with 1 M NaOH (3 × 20 mL) and H_2O (20 mL) and dried with $MgSO_4$. Removal of the solvent, followed by column chromatography (SiO_2, eluent 10% EtOH in CH_2Cl_2) afforded **14**–CTV0DGA. Yield 0.20 g (62%); mp 143–145 °C; MALDI-TOF-MS: *m*/*z* 835.0 ($[M + H]^+$, calc. 835.4); ^{1}H NMR δ: 8.85 (s, 3H, NH), 8.41 (s, 3H, ArH), 6.96 (s, 3H, ArH), 4.77 (d, 3H, J = 13.6 Hz, ArC*H*HAr), 4.28 (s, 6H, NHCOCH_2O), 4.16 (d, 6H, COCH_2O), 3.87 (s, 9H, ArOCH_3), 3.63 (d, 3H, J = 13.6 Hz, ArC*H*HAr), 2.97 (s, 18H, NCH_3); ^{13}C NMR δ: 168.0, 166.7, 147.2, 135.5, 131.3, 125.4, 121.0, 111.7, 71.3, 69.7, 56.0, 36.0, 35.5. Anal. Calc. for $C_{42}H_{54}N_6O_{12}$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.28; H, 6.46; N, 9.94%.

2,7,12-Trimethoxy-3,8,13-tris(*N*-phenyl-*N*-methylmalonamido)-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (14–CTV0MPMA). A solution of *N*-phenyl-*N*-methylmalonic acid (0.48 g, 2.5 mmol) and DCC (0.52 g, 2.5 mmol) in $CHCl_3$ (8 mL) was stirred for 1 h at rt. Subsequently, CTV0 **8** (0.17 g, 0.42 mmol) and a solution of Et_3N (0.25 g, 2.5 mmol) in $CHCl_3$ (7 mL) were added and the resulting mixture was stirred at 60 °C for 18 h. After cooling, the precipitate was removed by filtration and the filtrate was washed with H_2O (10 mL), 1 M HCl (2 × 10 mL), and brine (3 × 10 mL) and dried with $MgSO_4$. The solvent was evaporated under reduced pressure and the crude product was taken up into CH_2Cl_2 (10 mL). The formed precipitate was removed by filtration and the filtrate was purified by column chromatography (SiO_2, eluent 3% EtOH in CH_2Cl_2) followed by preparative TLC affording **14**–CTV0MPMA. Yield 0.10 g (27%); mp 181–184 °C; MALDI-TOF-MS: *m*/*z* 931.9 ($[M + H]^+$, calc. 931.4); ^{1}H NMR δ: 9.91 (s, 3H, NH), 8.36 (s, 3H, ArH), 7.34–7.45 (m, 9H, PhH), 7.17 (d, 6H, J = 7.0 Hz, PhH), 6.92 (s, 3H, ArH), 4.74 (d, 3H, J = 13.6 Hz, ArC*H*HAr), 3.88 (s, 3H, ArOCH_3), 3.60 (d, 3H, J = 13.9 Hz, ArC*H*HAr), 3.31 (s, 9H, NCH_3), 3.20 (s, 3H, COC*H*HCO), 3.19 (s, 3H, COCH*H*CO); ^{13}C NMR δ: 168.4, 163.7, 147.4, 143.1, 135.2, 131.2, 130.1, 128.4, 127.1, 126.1, 121.1, 111.7, 56.1, 41.8, 37.6, 36.5. Anal. Calc. for $C_{54}H_{54}N_6O_9$: C, 69.66; H, 5.85; N, 9.03. Found: C, 69.77; H, 5.83; N, 9.10%.

2,7,12-Trimethoxy-3,8,13-tris(((diphenylphosphoryl)acetamido)propoxy)-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (15–CTV3CMPO). To a suspension of **11a** (0.30 g, 0.37 mmol) in $CHCl_3$ (25 mL) was added Et_3N (0.32 mL, 2.23 mmol). The mixture was heated to 40 °C under stirring until the reactants were dissolved. To this solution was added the *p*-nitrophenyl activated ester of CMPO (0.85 g, 2.23 mmol) and the mixture was stirred for 18 h at 50 °C. The mixture was allowed to cool to rt and washed with 1 M NaOH (3 × 20 mL). The organic layer was dried with $MgSO_4$ and the solvent was removed under reduced pressure. Column chromatography (SiO_2, eluent 6.5%–7.5% EtOH in CH_2Cl_2) afforded **15**–CTV3CMPO. Yield 0.23 g (49%); mp 99–103 °C; MALDI-TOF-MS: *m*/*z* 1305.6 ($[M]^+$, calc. 1305.5); ^{1}H NMR δ: 7.61–7.76 (m, 12H, PhH), 7.4–7.47 (m, 12H, PhH), 7.22–7.25 (m, 9H, NH + PhH), 6.87 (s, 3H, ArH), 6.82 (s, 3H, ArH), 4.77 (d, 3H, J = 13.9 Hz, ArC*H*HAr), 3.73–3.94 (m, 6H, ArOCH_2), 3.81 (s, 9H, ArOCH_3), 3.55 (d, 3H, J = 13.9 Hz, ArC*H*HAr), 3.28–3.32 (m, 12H, CH_2N + CH_2P), 1.81 (q, 6H, J = 6.2 Hz, CH$_2$CH_2CH$_2$); ^{13}C NMR δ: 164.9, 148.2, 146.9, 132.5, 132.2, 132.0, 130.9, 130.7, 128.8, 128.7, 128.5, 115.3, 113.9, 67.3, 56.5, 39.6, 37.3, 36.4, 28.8. Anal. Calc. for $C_{75}H_{78}N_3O_{12}P_3$: C, 68.96; H, 6.02; N, 3.22. Found: C, 69.03; H, 5.94; N, 3.17%.

2,7,12-Trimethoxy-3,8,13-tris((*N*,*N*-dimethyl-3-oxaglutaramido)propoxy)-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (15–CTV3DGA). To a suspension of **11a** (0.30 g, 0.37 mmol) in $CHCl_3$ (25 mL) was added Et_3N (0.32 mL, 2.23 mmol). The mixture was heated to 40 °C under stirring until the reactants were dissolved. To this solution was added the *p*-nitrophenyl activated ester of DGA (0.59 g, 2.23 mmol) and the mixture was stirred for 18 h at 50 °C. The mixture was allowed to cool to rt and washed with 1 M NaOH (3 × 20 mL). The organic layer was dried with $MgSO_4$ and the solvent was removed under reduced pressure. Column chromatography (SiO_2, eluent 20% EtOH in CH_2Cl_2 followed by rinsing with AcOH–MeOH–CH_2Cl_2 3.5 : 10 : 86.5) afforded **15**–CTV3DGA. Yield 0.30 g (78%); mp 94–96 °C; MALDI-TOF-MS: *m*/*z* 1009.0 ($[M + H]^+$, calc. 1008.5); ^{1}H NMR δ: 7.83 (t, 3H, J = 5.5 Hz, NH), 6.86 (s, 3H, ArH), 6.82 (s, 3H, ArH), 4.71 (d, 3H, J = 13.9 Hz, ArC*H*HAr), 4.16 (s, 6H, NHCOCH_2O), 3.94–4.09 (m, 12H, ArOCH_2 + COCH_2O), 3.80 (s, 9H, ArOCH_3), 3.41–3.54 (q + d, 9H, CH_2NH + ArC*H*HAr), 2.75 (s, 9H, NCH_3), 2.74 (s, 9H, NCH_3), 2.02 (q, 6H, J = 6.3 Hz, CH$_2$CH_2CH$_2$); ^{13}C NMR δ: 169.5, 168.5, 148.5, 147.0, 132.6, 131.9, 116.1, 113.9, 71.8, 69.7, 67.8, 56.3, 36.3, 35.5, 35.2, 29.2. Anal. Calc. for $C_{51}H_{72}N_6O_{15}$: C, 60.70; H, 7.19; N, 8.33. Found: C, 60.78; H, 7.12; N, 8.40%.

2,7,12-Trimethoxy-3,8,13-tris((pyridine-2-carbonylamino)-propoxy)-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (15–CTV3PICO). To a suspension of **11a** (0.23 g, 0.40 mmol) in $CHCl_3$ (15 mL) was added Et_3N (0.32 mL, 2.23 mmol). The mixture was heated to 40 °C under stirring until the reactants were dissolved. To this solution was added the pentafluorophenol activated ester of PICO (0.69 g, 2.38 mmol) and the mixture was stirred for 18 h at 50 °C. The mixture was allowed to cool to rt and washed with 1 M NaOH (3 × 10 mL). The organic layer was dried with $MgSO_4$ and the solvent was removed under reduced pressure. Column chromatography (SiO_2, eluent 2%–3.5% EtOH in CH_2Cl_2) afforded **15**–CTV3PICO as a white solid. Yield 0.31 g (88%); mp 61–64 °C; MALDI-TOF-MS: *m*/*z* 895.6 ($[M + H]^+$, calc. 895.4); ^{1}H NMR δ: 8.50 (d, 3H, J = 4.0 Hz, PhH), 8.28 (s, 3H, NH), 8.18 (d, 3H, J = 8.1 Hz, PhH), 7.82 (t, 3H, J = 8.4 Hz, PhH), 7.39 (t, 3H, J = 6.2 Hz, PhH), 6.90 (s, 3H, PhH), 6.81 (s, 3H, H), 4.74 (d, 3H, J = 13.6 Hz, ArC*H*HAr), 4.07–4.76 (m, 6H, ArOCH_2), 3.74 (s, 9H, ArOCH_3), 3.82 (d, 3H, J = 13.9 Hz, ArC*H*-HAr), 2.12 (q, 6H, J = 6.4 Hz, CH$_2$CH_2CH$_2$); ^{13}C NMR δ: 164.4, 148.5, 148.1, 147.9, 146.8, 137.1, 132.6, 131.7, 125.9, 121.9, 116.1, 113.6, 67.5, 56.0, 36.6, 36.3, 29.2. Anal. Calc. for $C_{51}H_{54}N_6O_9$: C, 68.44; H, 6.08; N, 9.39. Found: C, 68.34; H, 5.99; N, 9.39%.

2,7,12-Trimethoxy-3,8,13-tris((*N*-phenyl-*N*-methylmalonamido)propoxy)-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (15–CTV3MPMA). A solution of *N*-phenyl-*N*-methylmalonic acid (0.31 g, 1.6 mmol) and DCC (0.34 g, 1.6 mmol) in $CHCl_3$ (5 mL) was stirred for 1 h at rt. Subsequently, a solution of **11a** (0.25 g, 0.27 mmol) and Et_3N (0.22 mL, 1.6 mmol) in $CHCl_3$ (5 mL) was added and the resulting mixture was stirred at 60 °C for 48 h. After cooling, the precipitate was removed by filtration and the filtrate was washed with H_2O (10 mL), brine (10 mL), 1 M HCl (2 × 10 mL), and dried with $MgSO_4$. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (SiO_2, eluent 5%–7.5% EtOH in CH_2Cl_2) giving **15**–CTV3MPMA as a white solid. Yield 0.27 g (89%); mp 82–87 °C; MALDI-TOF-MS: *m*/*z* 1105.3 ($[M + H]^+$, calc. 1105.5); ^{1}H NMR δ: 7.85 (br s, 3H, NH), 7.29–7.42 (m, 9H, PhH), 7.16 (d, 6H, J = 7.0 Hz, PhH), 6.87 (s, 3H, ArH), 6.84 (s, 3H, ArH), 4.74 (d, 3H, J = 13.6 Hz, ArC*H*HAr), 3.94–4.10 (m, 6H, $ArOCH_2$), 3.80 (s, 9H, $ArOCH_3$), 3.54 (d, 3H, J = 13.9 Hz, ArC*H*HAr), 3.44 (q, 6H, J = 6.2 Hz, CH_2NH), 3.26 (s, 9H, NCH_3), 3.05 (s, 6H, $COCH_2CO$), 2.00 (q, 6H, J = 6.2 Hz, $CH_2CH_2CH_2$); ^{13}C NMR δ: 168.4, 166.3, 148.5, 146.9, 143.1, 132.6, 131.9, 130.0, 128.3, 127.0, 116.0, 113.9, 67.7, 56.3, 40.7, 37.4, 36.9, 36.4, 29.1. Anal. Calc. for $C_{63}H_{72}N_6O_{12}$: C, 68.46; H, 6.52; N, 7.60. Found: C, 68.52; H, 6.53; N, 7.64%.

2,7,12-Trimethoxy-3,8,13-tris(((diphenylphosphoryl)acetamido)hexyloxy)-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (16–CTV6CMPO). A suspension of **13** (0.45 g, 0.64 mmol) and the *p*-nitrophenyl activated ester of CMPO (0.81 g, 2.12 mmol) in $CHCl_3$ (10 mL) was stirred at 50 °C for 18 h. The reaction mixture was washed with 1 M NaOH (3 × 10 mL) and H_2O (10 mL). The mixture was dried with $MgSO_4$. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (SiO_2, eluent 10% EtOH in CH_2Cl_2) to afford **16**–CTV6CMPO. Yield 0.52 g (56%); mp 179–180 °C; MALDI-TOF-MS: *m*/*z* 1431.4 ($[M]^+$, calc. 1431.6); ^{1}H NMR δ: 7.69–7.76 (m, 12H, PhH), 7.46–7.52 (m, 18H, PhH), 7.34 (s, 3H, NH), 6.82 (s, 6H, ArH), 4.74 (d, 3H, J = 13.6 Hz, ArC*H*HAr), 3.84–3.98 (m, 6H, $ArOCH_2$), 3.80 (s, 9H, $ArOCH_3$), 3.53 (d, 3H, J = 13.9 Hz, ArC*H*HAr), 3.29 (d, 6H, J = 12.5 Hz, CH_2CO), 3.19 (q, 6H, J = 6.5 Hz, CH_2NH), 1.70 (q, 6H, J = 6.9 Hz, $ArOCH_2CH_2$), 1.30–1.45 (m, 18H, $CH_2CH_2CH_2$); ^{13}C NMR δ: 164.6, 148.2, 147.1, 132.6, 132.0, 132.0, 130.9, 130.7, 130.1, 129.0, 128.8, 115.3, 113.8, 69.1, 56.3, 39.8, 38.0, 36.4, 29.1, 26.4, 25.6. Anal. Calc. for $C_{84}H_{96}N_3O_{12}P_3$: C, 70.43; H, 6.75; N, 2.93. Found: C, 70.46; H, 6.76; N, 2.95%.

2,7,12-Trimethoxy-3,8,13-tris((*N*,*N*-dimethyl-3-oxaglutaramido)hexyloxy)-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (16–CTV6DGA). A suspension of **13** (0.45 g, 0.64 mmol) and the *p*-nitrophenyl activated ester of DGA (0.56 g, 2.12 mmol) in $CHCl_3$ (10 mL) was stirred at 50 °C for 18 h. The reaction mixture was washed with 1 M NaOH (3 × 10 mL) and H_2O (10 mL). The mixture was dried with $MgSO_4$. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (SiO_2, eluent 12% EtOH in CH_2Cl_2) to give **16**–CTV6DGA. Yield 0.37 g (52%); mp 163–164 °C; MALDI-TOF-MS: *m*/*z* 1134.8 ($[M]^+$, calc. 1134.6); ^{1}H NMR δ: 7.60 (s, 3H, NH), 6.82 (s, 3H, ArH), 6.81 (s, 3H, ArH), 4.73 (d, 3H, J = 13.6 Hz, ArC*H*HAr), 4.20 (s, 6H, $NHCOCH_2$), 4.05 (s, 6H, $COCH_2$), 3.89–4.00 (m, 6H, $ArOCH_2$), 3.80 (s, 9H, $ArOCH_3$), 3.51 (d, 3H, J = 13.6 Hz, ArC*H*HAr), 3.28 (q, 6H, J = 6.6 Hz, CH_2NH), 2.89 (s, 9H, NCH_3), 2.81 (s, 9H, NCH_3), 1.78 (q, 6H, J = 7.0 Hz, $ArOCH_2CH_2$), 1.56 (q, 6H, J = 7.1 Hz, CH_2CH_2N), 1.35–1.48 (m, 12H, CH_2CH_2); ^{13}C NMR δ: 169.3, 168.6, 148.2, 147.3, 132.0, 131.9, 115.3, 114.0, 71.9, 69.7, 69.2, 56.3, 38.8, 36.4, 35.5, 35.4, 29.3, 29.1, 26.6, 25.7. Anal. Calc. for $C_{60}H_{90}N_6O_{15}$; C, 63.47; H, 7.99; N, 7.40. Found: C, 63.44; H, 8.03; N, 7.33%.

2,7,12-Trimethoxy-3,8,13-tris(((pyridine-2-carbonyl)amino)-hexyloxy)-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (16–CTV6PICO). A suspension of **13** (0.45 g, 0.64 mmol) and the pentafluorophenol activated ester of PICO (0.33 g, 2.12 mmol) in $CHCl_3$ (10 mL) was stirred for 18 h at 50 °C. The mixture was allowed to cool to rt and washed with 1 M NaOH (3 × 10 mL). The organic layer was dried with $MgSO_4$ and the solvent was removed under reduced pressure. Column chromatography (SiO_2, eluent 6% EtOH in CH_2Cl_2) afforded **16**–CTV6PICO. Yield 0.28 g (43%); mp 134–135 °C; MALDI-TOF-MS: *m*/*z* 1021.2 ($[M + H]^+$, calc. 1021.5); ^{1}H NMR δ: 8.50 (d, 3H, J = 3.3 Hz, PhH), 8.18 (d, 3H, J = 7.7 Hz, PhH), 8.04 (br s, 3H, NH), 7.81 (t, 3H, J = 7.7 Hz, PhH), 7.37 (t, 3H, J = 6.0 Hz, PhH), 6.82 (s, 3H, ArH), 6.80 (s, 3H, ArH), 4.73 (d, 3H, J = 13.6 Hz, ArC*H*HAr), 3.88–4.03 (m, 6H, $ArOCH_2$), 3.79 (s, 9H, $ArOCH_3$), 3.43–3.53 (m, 9H, ArC*H*HAr + CH_2NH), 1.78–1.80 (m, 6H, $ArOCH_2CH_2$), 1.63–1.67 (m, 6H, CH_2CH_2NH), 1.47–1.48 (m, 12H, CH_2CH_2); ^{13}C NMR δ: 164.1, 150.0, 148.2, 147.9, 147.2, 137.2, 132.0, 131.9, 125.9, 122.0, 115.3, 114.0, 69.2, 56.2, 39.2, 36.4, 29.5, 29.1, 26.6, 25.7. Anal. Calc. for $C_{60}H_{72}N_6O_9$: C, 70.57; H, 7.11; N, 8.23. Found: C, 70.60; H, 7.13; N, 8.24%.

2,7,12-Trimethoxy-3,8,13-tris((*N*-phenyl-*N*-methylmalonamido)hexyloxy)-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (16–CTV6MPMA). A solution of *N*-phenyl-*N*-methylmalonic acid (0.50 g, 2.6 mmol) and DCC (0.53 g, 2.6 mmol) in $CHCl_3$ (8 mL) was stirred for 1 h at rt. Subsequently, a solution of **13** (0.30 g, 0.43 mmol) and Et_3N (0.36 mL, 2.6 mmol) in $CHCl_3$ (7 mL) was added and the resulting mixture was stirred at 60 °C for 48 h. After cooling, the precipitate was removed by filtration and the filtrate was washed with H_2O (10 mL), brine (10 mL), 1 M HCl (2 × 10 mL), and dried with $MgSO_4$. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (SiO_2, gradient elution 3.5–4% EtOH in CH_2Cl_2) to give **16**–CTV6MPMA. Yield 0.32 g (60%); mp 150–154 °C; MALDI-TOF-MS: *m*/*z* 1231.9 ($[M + H]^+$, calc. 1231.7); ^{1}H NMR δ: 7.86 (br s, 3H, NH), 7.31–7.43 (m, 9H, PhH), 7.15 (d, 6H, J = 7.0 Hz, PhH), 6.83 (s, 3H, ArH), 6.81 (s, 3H, ArH), 4.73 (d, 3H, J = 13.6 Hz, ArC*H*HAr), 3.88–4.02 (m, 6H, $ArOCH_2$), 3.80 (s, 9H, $ArOCH_3$), 3.52 (d, 3H, J = 13.9 Hz, ArC*H*HAr), 3.21–3.27 (m, 15H, NCH_3, NCH_2), 3.05 (s, 6H, $COCH_2CO$), 1.79 (q, 6H, J = 6.8 Hz, $ArOCH_2CH_2$),

1.38–1.59 (m, 18H, $CH_2CH_2CH_2$); ^{13}C NMR δ: 168.8, 165.9, 148.3, 147.3, 142.9, 132.0, 131.9, 130.0, 128.3, 126.9, 115.3, 114.0, 69.2, 56.3, 40.2, 39.2, 37.4, 36.4, 29.3, 29.1, 26.7, 25.7. Anal. Calc. for $C_{72}H_{90}N_6O_{12}$: C, 70.22; H, 7.37; N, 6.82. Found: C, 70.13; H, 7.34; N, 6.90%.

4-*tert*-Butylbenzamido-4-*tert*-butyloxycarbonylaminopropyl-1,7-bis(*tert*-butyloxycarbonylamino)heptane (18). A solution of **17** (1.94 g, 3.9 mmol), *tert*-butylbenzoyl chloride (0.76 g, 3.9 mmol), and Et_3N (5.4 mL, 38.7 mmol) was stirred in toluene (40 mL) at 90 °C for 5 h. Part of the solvent was evaporated under reduced pressure, whereupon the residue was slowly cooled to −20 °C. White crystals were formed which were filtered off and washed with hexane (2 × 20 mL) giving C-pivot **18**. Yield 1.2 g (47%); mp 174–176 °C; FAB-MS: m/z 663.5 ([M + H]$^+$, calc. 663.5); ^{1}H NMR δ: 7.65 (d, 2H, J = 8.4 Hz, PhH), 7.42 (d, 2H, J = 6.6 Hz, PhH), 5.65 (s, 1H, NH), 4.64 (s, 3H, NH), 3.07–3.13 (q, 6H, J = 6.3 Hz, CH_2NH), 1.76–1.82 (m, 6H, $CH_2CH_2CH_2$), 1.39–1.50 (m, 6H, CCH_2CH_2), 1.42 (s, 27H, $OC(CH_3)_3$), 1.33 (s, 9H, $C(CH_3)_3$); ^{13}C NMR δ: 166.8, 156.1, 154.9, 132.4, 129.0, 128.2, 79.2, 40.8, 34.9, 32.3, 31.1, 28.4, 23.9. Anal. Calc. for $C_{36}H_{62}N_4O_7$: C, 65.23; H, 9.43; N, 8.45. Found: C, 65.24; H, 9.36; N, 8.48%.

4-*tert*-Butylbenzamido-4-(((diphenylphosphoryl)acetamido) propylamino)-1,7-bis((diphenylphosphoryl)acetamido)heptane (20–pivCMPO). To a solution of C-pivot **18** (2.80 g, 4.2 mmol) in CH_2Cl_2 (10 mL) was added TFA (10 mL) and the resulting solution was stirred for 1 h at rt. The solution was quenched by the addition of Et_2O (60 mL) whereupon a precipitate was formed. The precipitate was filtered off, washed extensively with Et_2O and dried *in vacuo* to give 2.7 g (91%) of the TFA salt of 4-*tert*-butylbenzamido-4-aminopropyl-1,7-heptanediamine **19** as a white foam. HRM, FAB-MS: m/z 725.620 ([M − 2H$^+$], calc. 725.614); ^{1}H NMR δ: (CD_3OD) 6.31 (d, 2H, J = 7.4 Hz, PhH), 6.07 (d, 2H, J = 8.4 Hz, PhH), 1.88 (s, 3H, NH), 1.51–1.56 (t, 6H, J = 6.0 Hz, CH_2NH), 0.48–0.53 (m, 6H, $CH_2CH_2CH_2$), 0.27 (br, 6H, CCH_2CH_2), 0.086 (s, 9H, $C(CH_3)_3$). A solution of the TFA salt of **19** (0.40 g, 0.6 mmol), the activated *p*-nitrophenol ester of CMPO (0.71 g, 1.9 mmol), and Et_3N (0.09 mL, 6 mmol) in $CHCl_3$ (30 mL) was refluxed for 18 h. The organic layer was washed with 1 M NaOH (6 × 15 mL) and H_2O (15 mL), whereupon it was dried with $MgSO_4$. Column chromatography (SiO_2, 1 : 1 EtOH–EtOAc) afforded **20**–pivCMPO. Yield 0.39 g (59%); mp 152–153 °C; FAB-MS: m/z 1111.6 ([M + Na]$^+$) and 1127.6 ([M + K]$^+$, calc. 1111.5 and 1127.6, respectively); ^{1}H NMR δ: 7.41–7.75 (m, 34H, PhH), 5.45 (s, 1H, NH), 3.68–3.75 (q, 6H, J = 7.0 Hz, CH_2NH), 3.50 (d, 6H, J = 12.6 Hz, $C(O)CH_2P(O)$), 3.15 (s, 3H, NH), 1.51–1.54 (m, 6H, $CH_2CH_2CH_2$), 1.34 (s, 9H, $C(CH_3)_3$), 1.21–1.26 (t, 6H, J = 6.9 Hz, CCH_2CH_2); ^{13}C NMR δ: 166.7, 164.6, 154.7, 132.3, 131.0, 130.8, 130.7, 128.8, 128.7, 126.7, 125.3, 58.3, 39.7, 39.4, 38.5, 34.8, 32.1, 31.2. Anal. Calc. for $C_{63}H_{71}N_4O_7P_3$: C, 69.47; H, 6.57; N, 5.14. Found: C, 69.44; H, 6.56; N, 5.18%.

Extractions

Solvent phase extractions. The ligands were dissolved in the appropriate organic solvent (0.25 mL) and shaken (1800 rpm) with the appropriate aqueous solution (0.25 mL) at ambient temperature (22–24 °C) for 60 min for equilibration in a 2 mL screw cap vial. Subsequently, the two layers were separated by centrifugation (5 min, 1600 rpm). 0.15 mL of each layer was pipetted out into vials and positioned for γ-ray measurement. The gamma-activity was determined by measuring for 1 h with a Germanium High Purity Ge(HP)-detector. The reported D_M values are the averages of at least two experiments. The errors in the extraction percentages of the duplicate experiments are less than 4%. In the region $5\% > E > 95\%$ the error in the D_M values is larger since, for example, an extraction of 95 ± 1% results in a D_M of 19 ± 5.

Tracer solutions. In each extraction between 200 Bq and 600 Bq of ^{241}Am and ^{152}Eu, depending on the D_M values of the ligands, was used. Where necessary, the concentration of Eu^{3+} was adjusted by addition of a stable isotope of europium. The ^{241}Am and ^{152}Eu isotopes were used from NRG (Nuclear Research & Consultancy Group) stock.

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